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Polyester Resin Composition for Calendering

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(54) [Title of the Invention]

Polyester Resin Composition for Calendering

(57) [Summary]

[Object] To provide a polyester resin composition for calendering that does not cause the resin to sag during calendering.

[Means of Achievement] A polyester resin composition for calendering, characterized in that the tensile storage modulus is 10^7 Pa or higher at 25°C, and the temperature region in which the tensile storage modulus ranges from 10^7 Pa to 10^6 Pa is 60°C and higher. In particular, a polyester resin composition for calendering that satisfies the storage modulus as a result of containing 0.1 to 5 parts of polyisocyanate per 100 parts of polyester.

[Claims]

[Claim 1] A polyester resin composition for calendering, characterized in that the tensile storage modulus is 1×10^7 Pa or higher at 25°C, and the temperature region in which the tensile storage modulus ranges from 1×10^7 Pa to 1×10^6 Pa is 60°C and higher.

[Claim 2] The polyester resin composition for calendering according to Claim 1, wherein 0.1 to 5 parts of polyisocyanate are contained per 100 parts of polyester.

[Claim 3] The polyester resin composition for calendering according to Claim 2, wherein the polyisocyanate described in Claim 2 is a tolylene diisocyanate dimer.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a polyester resin composition for calendering that is useful in industrially machined sheets and films, has good roll release properties when polyester calendering is performed, and in particular has exceptional sheet take-up during calendering.

[0002]

[Prior Art] Vinyl chloride sheets (and films) are typically inexpensive and have exceptional workability, which lends them extensive usability in a variety of applications. Methods for working such sheets include extrusion molding and calender molding, but the latter is more widespread due to the better dimensional control provided over the thickness and width of the sheets provided, and greater suitability for mass production than with extrusion molding. Finished vinyl chloride sheets have properties (transparency, flame resistance, electrical insulability, durability, hardness control, and the like) that are superior to those of other resins. However, recent concerns relating to dioxin emissions when vinyl chloride is incinerated as well as to environmental hormones produced by means of plasticizers have prompted calls for alternative resin materials to be used. Polyester is a strong choice for such a substitute material in light of its physical characteristics and cost, and has accordingly become the subject of various studies.

[0003] However, suitability for calender molding remains a major problem that prevents vinyl chloride from being replaced by polyester. Ease of workability has been the reason extrusion

molding is extensively used as a method for manufacturing sheets and films from polyester resins. When such polyester resins are calendered, relatively high adhesive forces are encountered with the rolls during thermoplasticization, and the resins tend to adhere to the rolls, which complicates the molding procedure. Attempts have been made to add polyethylene waxes and other various lubricants based on hydrocarbons, higher fatty acids, higher alcohols, fatty acid amides, and esters to the resin in order to prevent its adhesion to the rolls, as has been proposed in e.g. Japanese Patent Application (Kokai) Laid Open Nos. 11-343353, 2000-136294, 2000-186191, 2000-302951, and 2001-64496. Adding such lubricants allows a resin sheet to be removed without adhering to the rolls; however, the weight of the sheet causes the resin to sag before the sheet has reached the cooling rolls in the subsequent step, thereby eliminating the inherent calendering property that allows sheets of good dimensional stability to be obtained.

[0004]

[Problems Intended to Be Resolved by the Invention] With the foregoing issues in view, it is an object of the present invention to provide a polyester resin composition for calendering that does not cause the resin to sag during calendering.

[0005]

[Means Used to Solve the Above-Mentioned Problems] The present inventors conducted diligent investigations in an attempt to achieve the aforementioned object, and as a result have proposed the following invention. In other words, the present invention resides in a polyester resin composition for calendering characterized in that the tensile storage modulus is 10^7 Pa or higher at 25°C, and the temperature region in which the tensile storage modulus ranges from 10^7 Pa to 10^6 Pa is 60°C and higher. In particular, the present invention resides in a polyester resin composition for calendering that satisfies the aforementioned storage modulus as a result of containing 0.1 to 5 parts of polyisocyanate per 100 parts of polyester. The polyisocyanate referred to above is preferably a tolylene diisocyanate dimer.

[0006] In the present invention, the tensile storage modulus is obtained by means of using a dynamic viscoelasticity measurement device to assess a resin in the form of a sheet. Typically, the sample sheet is 15 mm long (not including the gripping length), 4 mm wide, and approximately 1 mm thick, and the conditions for measurement involve fixing the frequency at 10 Hz and scanning the sheet at a temperature elevation rate of 20°C/min from -20°C until

measurement becomes impossible (a maximum of 250°C). There are no particular requirements specified for the method used to fabricate the sample sheet, but a smooth sheet may be obtained by means of sandwiching the polyester resin between polyimide films or other highly heat-resistant films, and then using a heat press or similar device set to a temperature at least 10°C higher than the softening point of the polyester resin to compress the assembly.

[0007] In the present invention, the tensile storage modulus of the polyester must be 10^7 Pa or higher at 25°C, and 10^7 Pa or lower at temperatures below 180°C. In the region at or below 250°C, the temperature region where the modulus ranges from 10^7 Pa to 10^6 Pa is 60°C and higher. A modulus of less than 10^7 Pa at 25°C is inappropriate for applications as a vinyl chloride sheet substitute, which is the object of the invention. Keeping the temperature region at 60°C and greater enables the appropriate viscoelasticity to be maintained in response to the distribution or variation in calender temperature control during calendering.

[0008] To obtain a polyester whose temperature region is 60°C or greater in accordance with the present invention, it is preferable that polyisocyanate be compounded and an appropriate chain length or crosslinked moiety be obtained to be able to accommodate polyesters of varied compositions. Viscoelasticity properties that remain stable during calendering may be obtained by means of adding 0.1 to 5 parts of polyisocyanate per 100 parts of polyester, though the amount will depend on the hydroxyl value of the polyester. Acceptable methods for compounding the polyisocyanate involve either using an extruder to bring about a reaction beforehand, or supplying the polyisocyanate together with the polyester directly to the calender rolls. The polyisocyanate may be a monomer, dimer, trimer, or alcohol adduct that is liquid or solid as well as aromatic, aliphatic, or alicyclic without particular limitation, though tolylene diisocyanate dimers are preferred.

[0009] Examples of dicarboxylic acids able to be used in the polyester of the present invention include terephthalic acid, isophthalic acid, orthophthalic acid, 1,5-naphthalic acid, 2,6-naphthalic acid, 4,4'-diphenyldicarboxylic acid, 2,2'-diphenyldicarboxylic acid, 4,4'-diphenylether dicarboxylic acid, and other aromatic dicarboxylic acids; and adipic acid, azelaic acid, sebacic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 4-methyl-1,2-cyclohexanedicarboxylic acid, dimer acid, hydrogenated dimer acid, and other aliphatic or alicyclic dicarboxylic acids. Examples of polyvalent carboxylic acid components that may be used include trimellitic anhydride and pyromellitic anhydride.

[0010] Examples of glycol components include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, diethylene glycol, dipolypropylene glycol, 2,2,4-trimethyl-1,3-pentanediol, cyclohexane dimethanol, tricyclodecane dimethanol, hydroxypivalic acid neopentyl glycol ester, ethylene oxide adducts and propylene oxide adducts of bisphenol A, ethylene oxide adducts and propylene oxide adducts of hydrogenated bisphenol A, 1,9-nonanediol, 2-methyloctanediol, 1,10-dodecanediol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol and other diols, and trimethylol propane and other polyhydric alcohols.

[0011] Examples of preferred compositions among combinations of the polyvalent dicarboxylic acids and polyhydric alcohols mentioned above for delivering vinyl chloride-like properties, transparency, workability, and low cost include terephthalic acid/isophthalic acid/ethylene glycol, terephthalic acid/ethylene glycol/neopentyl glycol, terephthalic acid/ethylene glycol/cyclohexane dimethanol, and terephthalic acid/isophthalic acid/ethylene glycol/1,4-butanediol.

[0012] Any known method may be used for manufacturing the polyester; e.g., the desired polyester may be obtained by means of subjecting the aforementioned dicarboxylic acids and diol components to esterification at 150 to 250°C, and subsequently performing polycondensation at 230 to 300°C under reduced pressure.

[0013] A lubricant, antioxidant, plasticizer, filler, UV absorber, photostabilizer, pigment, antistatic agent, or antibacterial agent may be compounded in addition to the polyester and polyisocyanate with the polyester resin composition for calendering of the present invention, provided that the viscoelasticity range specified in the claims is preserved. Examples of lubricants include polyolefin waxes, metal salts of organic phosphoric acid esters, organic phosphoric acid esters, higher fatty acids, higher fatty acid alcohols, and higher fatty acid esters, with the combined use of a polyolefin wax and a metal salt of an organic phosphoric acid ester being particularly recommended when the sheet transparency and release from the rolls are to be ensured at the same time. Antioxidants such as those based on phenols, phosphorus, and thioethers will inhibit the degradation brought about by means of thermal oxidation in polyether resins during calendering. Also, examples of fillers include talc and mica, while examples of plasticizers include acrylic oligomers and higher fatty acids.

[0014] The aforementioned components are blended with the polyester resin composition for calendering of the present invention using a Henschel mixer or other well-known blending apparatus, and the resulting mixture is kneaded with mixing rolls, warming rolls, a Banbury mixer, or the like, and is then supplied for calendering.

[0015]

[Working Examples]

The present invention is described in detail below with reference to working examples, but the present invention shall not be construed to be limited to these examples. The measurement values described in the examples have been obtained according to the methods described below.

[0016] Storage modulus

A sample of the polyester resin composition was placed on a heat press adjusted to 200°C, with a polyimide film ("Capton"; manufactured by DuPont-Toray Co., Ltd.) interposed therebetween. The sample was held in place for 20 sec under a pressure of 2 N/mm², resulting in a 1 mm-thick sheet sample. The sample was cut to a length of 15 mm (not including the gripping length) and a width of 4 mm, then positioned in a dynamic viscoelastometer ("DVA-200"; manufactured by I.T. Keisoku Seigyo). The measurements were performed in tensile mode. The conditions for measurement involved fixing the frequency at 10 Hz and scanning the sample at a temperature elevation rate of 20°C/min from -20°C until measurement becomes impossible (a maximum of 250°C).

[0017] Example detailing the manufacture of Polyester (A)

194 weight parts of dimethyl terephthalate ester, 102 weight parts of ethylene glycol, 57 weight parts of neopentyl glycol, and 0.1 weight parts of tetrabutyl titanate were added into a reaction vessel fitted with a stirrer, temperature gauge, and distillation cooler, and transesterified for two hours at 170 to 220°C. Once transesterification was complete, the reaction vessel temperature was elevated from 220 to 255°C while the pressure inside the system was gradually reduced, until a level of 5 torr had been attained at 255°C after 60 min. Polycondensation was subsequently performed for 30 min at 1 torr or less to obtain a sufficient molecular weight, whereupon the vacuum was broken in a nitrogen atmosphere. The resulting polyester was called "(A)." The terephthalic acid/ethylene glycol/neopentyl glycol (molar) ratio in the final

composition of polyester (A) was shown to be 100/65/35 by measuring the proton nuclear magnetic resonance spectrum after having dissolved the resin in heavy chloroform.

[0018] 1 part of tridecyl poly(oxyethylene)phosphate zinc salt, 0.5 parts of styrene-modified polyethylene wax, 0.4 parts of high-density polyethylene oxide wax, 0.1 parts of tetrakis-[methylene-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane, and 2 parts of 2,4-tolylene diisocyanate dimer ("Desmodur TT/G"; manufactured by Bayer Ltd.) were blended per 100 parts of polyester (A) in a beaker, and the resulting mixture (1) was kneaded on two 6-inch chilled rolls that had been set to 180°C. The mixing was performed for five minutes while any resin that had adhered to the chilled rolls was periodically removed with a spatula. The gap between the rolls was then set to 0.3 mm, and the product was taken up in the form of a sheet. The sheet takeup was smooth and was not accompanied by resin sag. The sheet was also transparent, and showed no coloration. Meanwhile, mixture (2), which had the same composition but did not contain any 2,4-tolylene diisocyanate, was similarly processed and extracted as a sheet. However, the resin had sagged, and a sheet of uniform thickness could not be obtained.

[0019] Samples of mixtures (1) and (2) that had been taken from the chilled rolls in advance were sandwiched between polyimide films and pressed with a heat press to yield sheets that were approximately 1 mm thick. Strips that were 20 mm long (15 mm long excluding the gripping length) and 4 mm wide were cut from these sheets, and used to measure the elastic tensile storage modulus. As shown in Fig. 1, the elastic storage modulus at 25°C was 10^7 Pa or higher in both cases, but the temperature region in which the elastic storage modulus ranged from 10^7 to 10^6 Pa was 90°C in mixture (1), and 45°C wide in mixture (2). Mixture (1) was within the range specified in the present patent, while mixture (2) was outside this range.

[0020]

[Effect of the Invention] As has been described in the foregoing, the polyester resin composition for calendering of the present invention shows good release from the rolls during calendering, and, in particular, shows an exceptional ability to be taken up as a sheet during calendering.

[Brief Description of the Drawings]

[Figure 1] Graph depicting the changes in the elastic storage moduli of mixtures (1) and (2)

